Temperature dependence of electronic states in $(TaSe_4)_2I$

A. Terrasi, M. Marsi, H. Berger, and G. Margaritondo
Institut de Physique Appliquée and Institut de Génie Atomique, Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

R. J. Kelley and M. Onellion
Physics Department, University of Wisconsin, Madison, Wisconsin 53706
(Received 8 February 1995)

Angle-resolved photoemissions studies were conducted on single-crystal $(TaSe_4)_2I$ samples above and below the charge-density-wave transition temperature (T_{CDW}) of 260 K. We observed a shift of the leading photoemission edge between 300 and 60 K consistent with resistivity measurements performed on the same sample: a band gap opens throughout the Brillouin zone below T_{CDW}. However, several aspects of the data are difficult to reconcile with any standard model.

The nature of the electronic ground state in quasi-one-dimensional systems has been of enduring interest.[1-5] Several recent reports[6-8] indicate that the ground state is not a Fermi liquid; many authors argue that the ground state is a Luttinger liquid.[9,10] Among the strongest spectroscopic evidence as to the nature of the ground state is the absence of a Fermi-Dirac distribution function line shape in photoemission.[11] This absence has been reported by several investigators on different quasi-one-dimensional systems.[6-8,11,12] Various explanations of the photoemission spectral features near the Fermi energy have been put forward, including phonon broadening,[13] a fluctuating charge-density-wave (CDW) (Refs. 14,15) with accompanying pseudogap,[16] and electron-electron correlations.[17]

We report on the results of a careful study of the temperature dependence of the valence band. We concentrated on the $(TaSe_4)_2I$ system, which exhibits a CDW instability at 260 K.[18] The crucial data are how the leading edge, and quasiparticle peaks, of the photoemission spectra change with temperature. We completely reproduced all aspects of the results discussed below six times, the number of times we studies this system.

Figure 1 illustrates angle-resolved photoemission spectra versus the wave vector for (a) photon electric field parallel to the conducting axis of the material, and (b) photon electric field perpendicular to the conducting axis of the material. Spectra were taken at room temperature, using a photon energy of 22 eV. Particularly noteworthy is that there are two dispersing quasiparticle band states, one observed for each of the two different photon polarizations. Since the standard theory of such a material indicates only one band state, this is a most surprising result. Because of this, we carefully reproduced the results six times to confirm them. We also rotated samples so that the sample conducting axis was at 45° with respect to the photon electric field. In such an orientation, we observed both of the electronic states illustrated in Figs. 1(a) and (b).

Figure 2 illustrates angle-resolved photoemission spectra versus wave vector, taken at 60 K, below the CDW transition temperature (T_{CDW}), for (a) photon electric-field vector parallel to the conducting axis of the material, and (b) photon electric-field vector perpendicular to the conducting axis of the material. A photon energy of 22 eV was used. Figure 2(c) illustrates the resistivity as a function of temperature. The spectra of Figs. 1 and 2 exhibit changes with temperature, in contrast to the unoccupied density of states (inverse photoemission) results reported by Ref. 15.

The changes with temperature include shifts in both the leading edge of the spectra and the dispersing quasiparticle features. The details are illustrated in Fig. 3 including the dispersing quasiparticle state at (a) wave vector 0.29 $Å^{-1}$ and (b) wave vector -0.14 $Å^{-1}$. Spectra taken at room temperature and low temperature are labeled. The spectra in Fig. 3 illustrate the shifts observed with temperature in both the leading edge and the dispersing quasiparticle peaks.

Figure 4 illustrates (a) the overall dispersion of the quasiparticle features with the wave vector, both at room temperature (open circles) and low temperature (closed circles), for the photon electric-field vector parallel to the conducting axis; (b) the overall dispersion of the quasiparticle features with the wave vector, both at room temperature (open circles) and low temperature (closed circles) for the photon electric-field vector perpendicular to the conducting axis; and (c) the shift of the leading edge between room and low temperatures with the wave vector. Note that the total-energy dispersion for either quasiparticle feature is 700–750 meV.

Several noteworthy points emerge from the data. The leading edge of the photoemission spectra shift to higher binding energy for all wave vectors [Figs. 3(b), 4(c)]. The data indicate a band-gap opening, not a pseudogap.[15] In fact, the size of the band-gap opening, 160±30 meV, agrees quantitatively with the estimate obtained from the resistivity data [Fig. 2(c)]: 160 meV. Note, however, that the gap of 160 meV implies a value of $2\Delta/kT_{CDW}=15$, well above the BCS mean field value of 3.5.[5] These data indicate that the highest-kinetic-energy photoemission spectral area is involved in electrical transport and resistivity.

Reference 15, which describes inverse photoemission

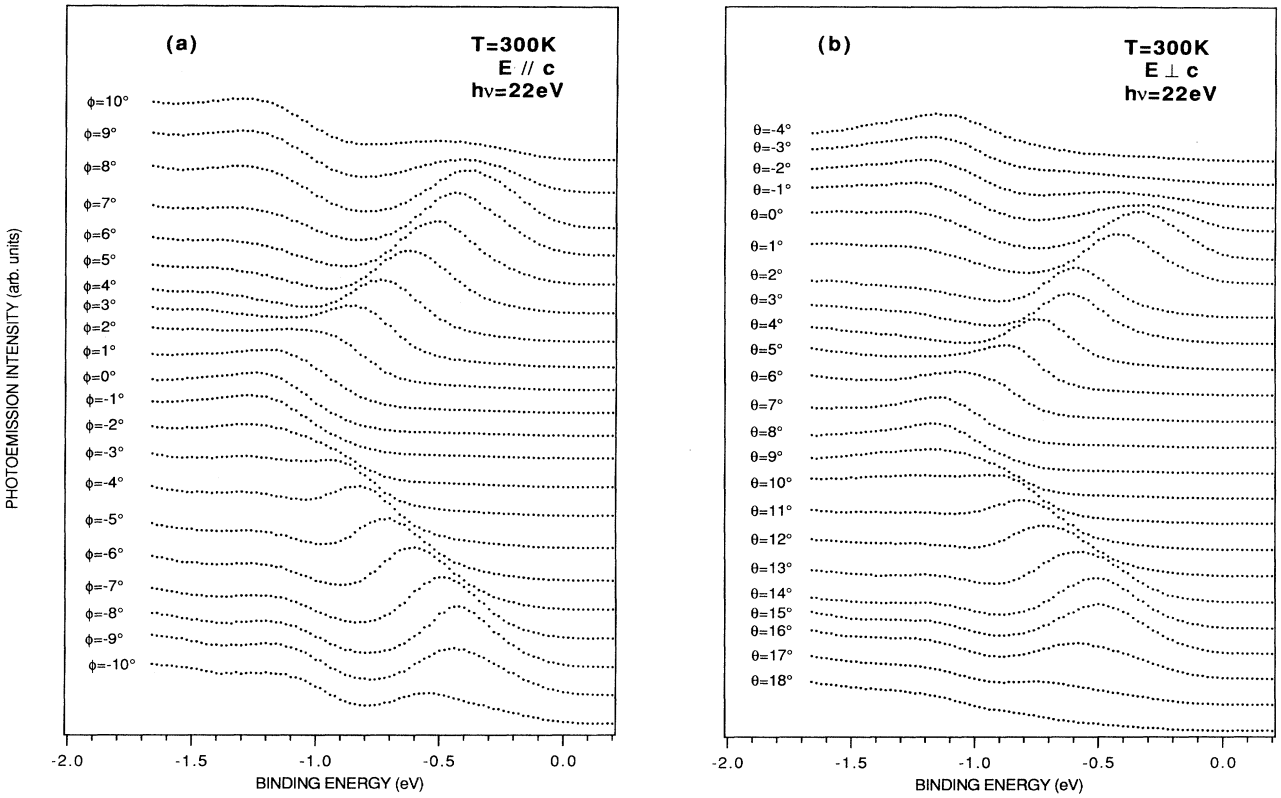

FIG. 1. Angle-resolved photoemission spectra taken using 22-eV photon energy, at room temperature, for photon electric field (a) parallel and (b) perpendicular to the conducting axis. The emission angle is along the conducting axis, with the surface normal defined as 0°.

results on samples from the same batch analyzed in the present work, reports that in the unoccupied density of states, there is no change in either the leading edge or the dispersing quasiparticle features, with temperature between 300 and 100 K. The hypothesis was proposed in Ref. 15 that a pseudogap of approximately 800 meV, caused by a fluctuating charge-density wave, might be present in this system for temperatures up to the mean-field temperature of 1000–1400 K. Such a pseudogap would provide an explanation for the lack of a Fermi-Dirac distribution function line shape.[15,16]

Our present results, however, do not support this hypothesis, since they indicate a real gap from both direct photoemission data and resistivity data. We note that, while a pseudogap of 800 meV is considerably larger than the optical-absorption edge of about 300 meV,[19] there are systems for which the pseudogap inferred from photoemission and inverse photoemission is larger than that measured in optical absorption.[15,20] Our data are, on the other hand, consistent with earlier reports,[6,7,11] that the shape of the photoemission leading edge is due to non-Fermi-liquid behavior, perhaps a Luttinger liquid ground state.

Comparison of the angle-resolved photoemission data in this report with the angle-resolved inverse photoemission data of Ref. 15 indicate that the electron-electron correlation effects are a major factor in this system. As Sawatzky and colleagues have noted[21] for other systems, a difference between adding and removing one electron, such as observed here for $(TaSe_4)_2I$, is an unambiguous indication of electron-electron correlation effects.

We compared our results, and those of Ref. 15, to optical-absorption data taken on samples of the same material.[19] These data lead to a consistent picture of the electronic band structure of this material, as illustrated in Fig. 5—which includes the band structure (a) above the CDW transition and (b) well below the CDW transition. Note again the shift of the leading edge in the occupied density of states that corresponds to the band-gap inferred from resistivity measurements.[22] In addition, the peak in the optical-absorption[19] data shifts 100 meV between 300 and 15 K, while our observation of the quasiparticle peak indicates a shift of 60–140 meV between 300 and 60 K.

These results are consistent, suggesting that the peak in the optical-absorption spectrum is due to the high density of states observed in photoemission. Note, however, that the absolute value of the peak in optical absorption[19] and in the quasiparticle binding energy (this report) differ by 100 meV, consistent with the observation in Ref. 15 that the absolute values in optical absorption tend to be less than those in photoemission and inverse photoemission. The authors of Ref. 19 attribute the nonzero optical absorption they observe at low photon energies to material

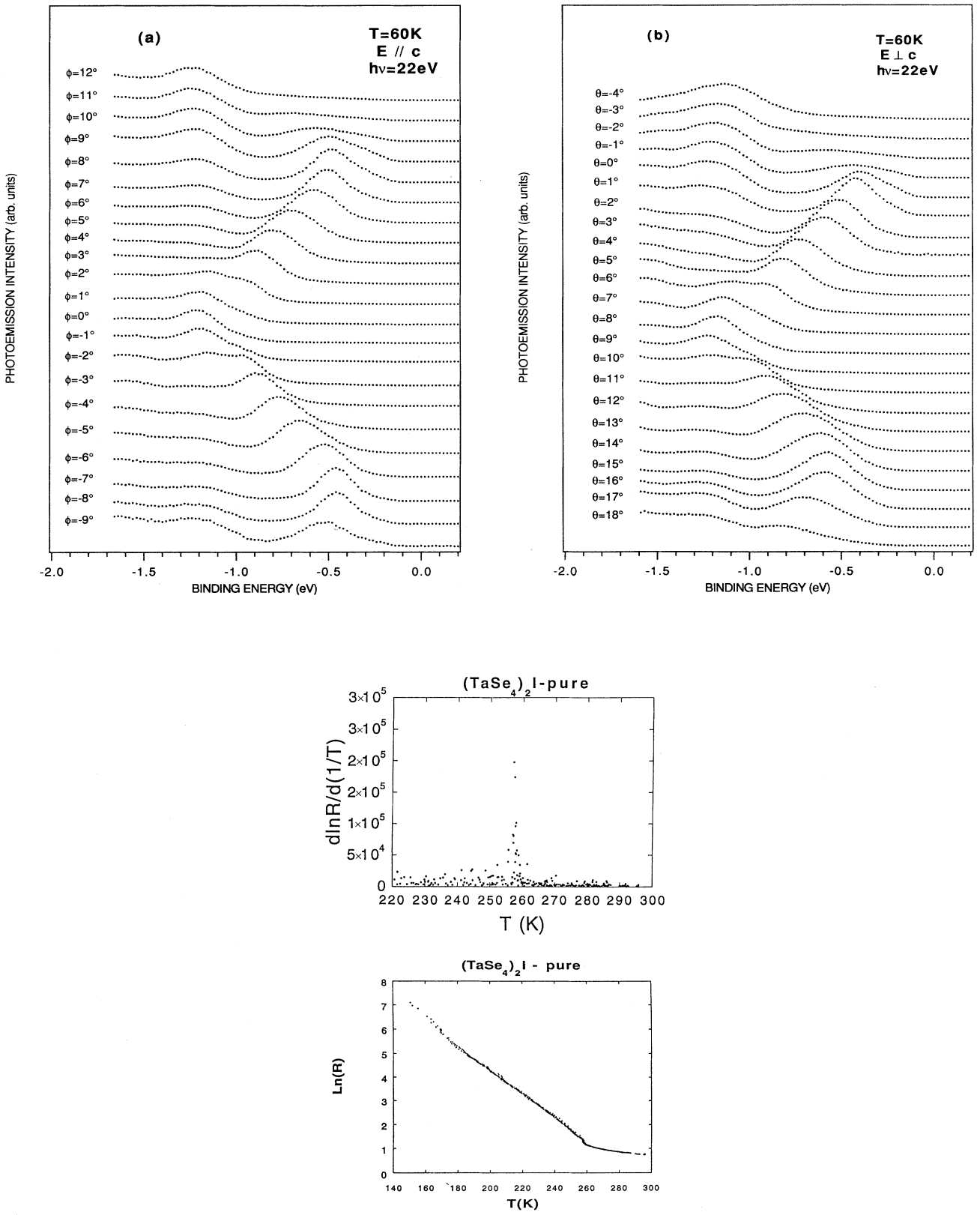

FIG. 2. Angle-resolved photoemission spectra taken using 22-eV photon energy, at 60 K, for photon electric field (a) parallel and (b) perpendicular to the conducting axis. The emission angle is along the conducting axis, with the surface normal defined as 0°. (c) Resistivity data as a function of the temperature.

defects. For that reason, the optical absorption at low photon energies would not be sensitive to the shift of the (low density of states) leading edge that we observe in photoemission [Fig. 4(c)].

There are two experimental observations for which we do not have a conclusive explanation. Note that the quasiparticle dispersion (Figs. 1, 2, 4) include two electronic states, both of which exhibit the periodicity of the charge-density-wave wave vector. One is observed when the photon electric-field vector is parallel to the material conducting axis, the other when the photon electric-field vector is perpendicular to the material conducting axis. This result is surprising because earlier reports[12] indicated only one dispersing quasiparticle peak. The data are consistent with quasiparticle band extrema at wave vectors of ± 0.27 Å^{-1}, with the two dispersing quasiparticle states both exhibiting a periodicity of 0.54 Å^{-1}. If only one band was observed, the result would be as expected for a half-filled band, where the Fermi wave vector, $K_F=(\pi/2L)$ (Ref. 5, Fig. 1).

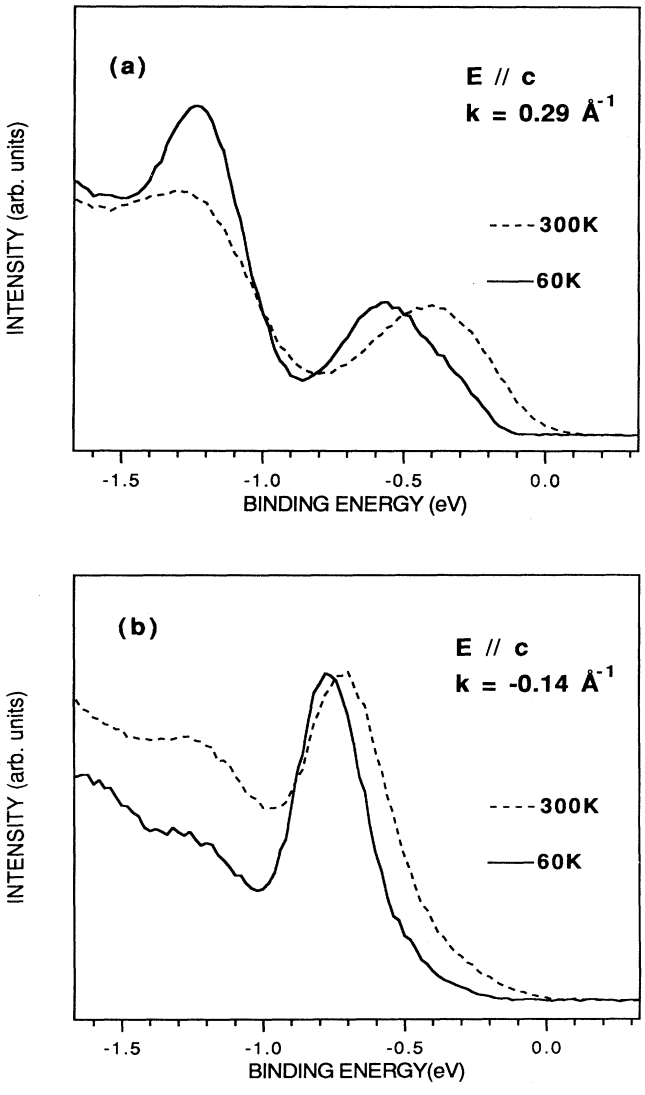

FIG. 3. Angle-resolved photoemission spectra taken using 22-eV photon energy, at wave vectors of (a) $k=0.29$ Å^{-1} and (b) $k=-0.14$ Å^{-1}. Spectra taken at 300 (dotted lines) and 60 K (solid lines) are illustrated. The data show both a shift of the leading edge and of the quasiparticle band binding energy with temperature.

The presence of two bands is thus an experimental fact. As to the reason for two bands, we can only speculate. A longitudinal charge-density wave will not produce two bands. In particular, because a longitudinal charge-density wave has even (gerade) symmetry, it cannot be involved in two bands when one exhibits even and the other odd symmetry. Note, though, that both bands have a periodicity consistent with the charge-density-wave wave vector.[15,18] In addition, note that the two bands appear to be noninteracting; their dispersion relations do not affect each other.

For this reason, the data indicate that the bands may arise from different origins. There are several reports in the literature[23–26] indicating that a quasi-one-dimensional system could support a transverse charge-density wave. Such a transverse charge-density wave would have the necessary (odd) symmetry to produce two bands, one of even and the other of odd symmetry. However, as pointed out in Ref. 25, transverse charge-density waves lead to a gapless Peierls transition, in contrast to the gap opening we observed [Fig. 4(c)]. None of the current models, therefore, fully explain our data.

In addition to observing two quasiparticle dispersing electronic states, the data indicate that the lowest binding energy of both of the quasiparticle states shifts to larger values by 100 ± 40 meV upon reducing the temperature below $T_{\rm CDW}$, the same shift reported by Ref. 19 for the peak in the optical absorption. The wave vectors at which we observe the largest shift of the quasiparticle feature are those of the CDW nesting. A shift to higher binding energy at such wave vectors would be the expected picture if the smallest binding energy was the Fermi energy. However, the smallest binding energy is, in fact, 400 ± 40 meV. Consequently, the fact that a quasiparticle dispersing state 400 meV below the Fermi energy exhibits a shift in binding energy with temperature is a most surprising result.

In summary, we have observed a shift of the leading edge of photoemission spectra to higher binding energy as the temperature is lowered below $T_{\rm CDW}$. The amount of the smaller shift is in quantitative agreement with the value expected from resistivity data, and implies a value of $2\Delta/kT_{\rm CDW}=15$. This value is well above the BCS value of 3.5, and indicates that fluctuations play a role in the observed properties of this system.[11] However, the quantitative agreement between photoemission and resistivity data to not support the hypothesis that fluctuations cause a pseudogap that accounts for the loss of photoemission spectral intensity near the Fermi edge. Instead, our data reinforce the arguments made earlier by other investigators[6,7,11] that the ground state of this system is not a Fermi liquid.

The shift with temperature in the photoemission data, coupled with the lack of observeable shift in inverse photoemission data as reported in Ref. 15, indicates that

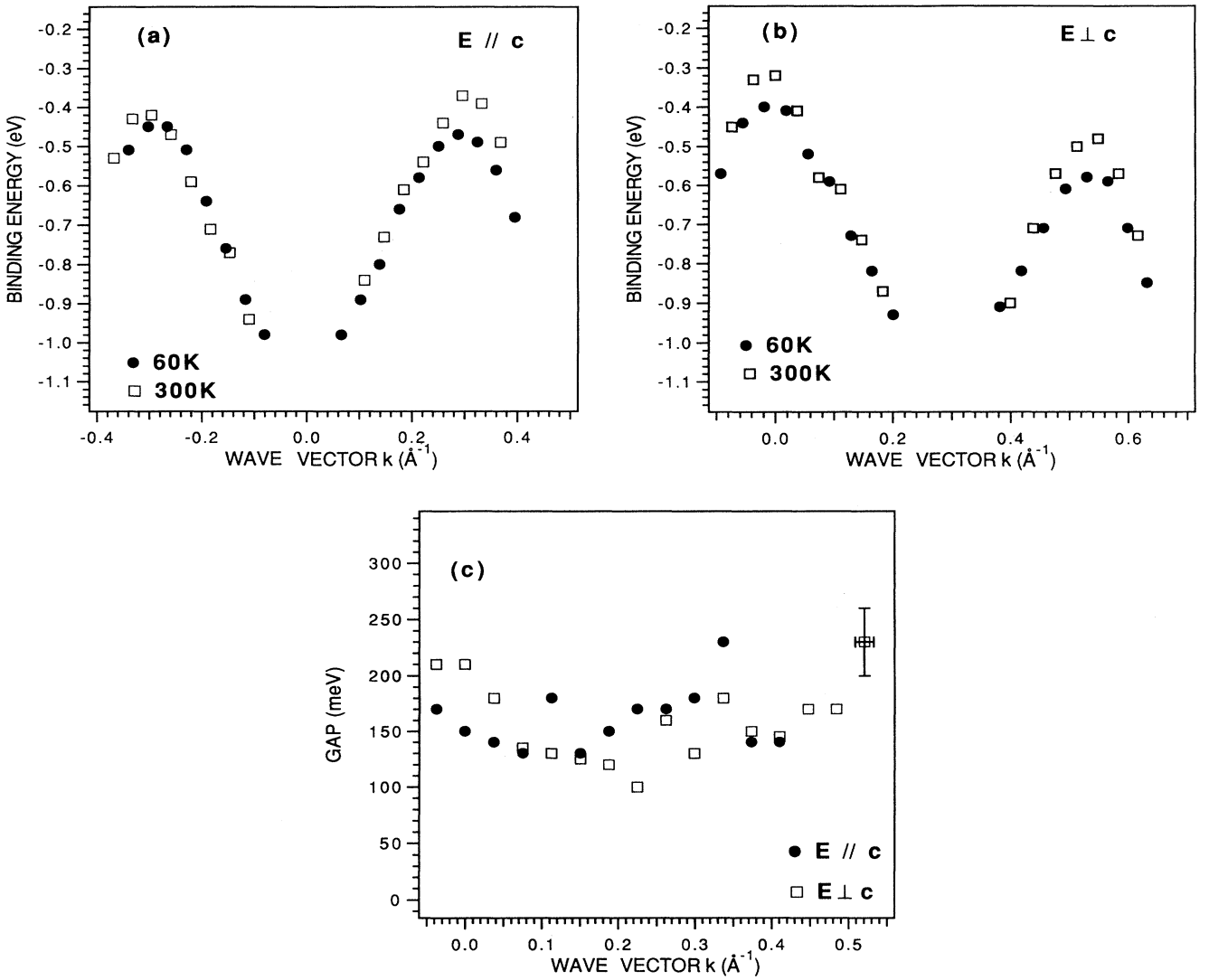

FIG. 4. (a) Dispersion relation for the quasiparticle band observed using the photon electric-field vector parallel to the conducting axis, both at 300 (open squares) and 60 K (closed circles); (b) corresponding quasiparticle dispersion relation for the photon electric field perpendicular to the conducting axis; (c) shift of the leading edge between 300 and 60 K for both the photon electric field parallel to (closed circles) and perpendicular to (open squares) the conducting axis. A photon energy of 22 eV was used throughout.

electron-electron correlations are playing a major role in this system. The shift of spectral features with temperature is not a rigid shift, again indicating that electron-electron correlation effects, rather than a rigid shift of the chemical potential (in a one-electron picture), are responsible for the shift.

The shift of the quasiparticle peak with temperature is in quantitative agreement with the shift of the peak in the optical-absorption data on the same material.[19] The agreement among resistivity (this work and Ref. 27), inverse photoemission,[15] optical absorption,[19] and photoemission data (present report) lead to the electronic band structure illustrated in Fig. 5.

Finally, there are two aspects of our data for which we cannot conclusively account. We have observed two

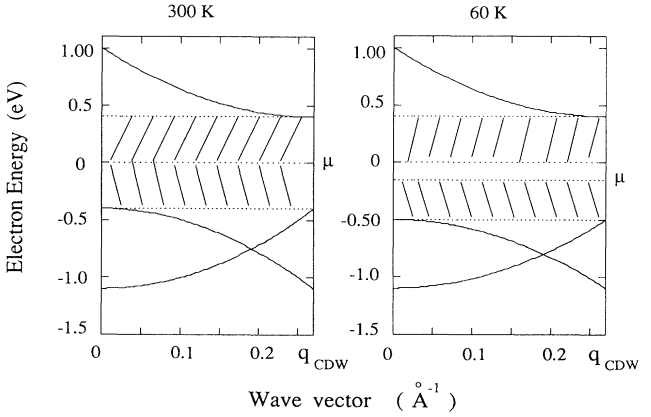

FIG. 5. Schematic band structure derived from our analysis.

dispersing quasiparticle states, rather than the one expected. We have observed a shift of the dispersing quasiparticle minimum binding energy to a higher value by 100 ± 40 meV when the temperature is lowered below T_{CDW}. Such a shift of a state 400 meV binding energy (at room temperature) is difficult to reconcile with any of the standard models of a CDW gap and/or a Luttinger liquid.

We benefitted from conversations with Douglas Purdie, Nick Shannon, Andrei Chubukov, Lazlo Forro, Robert Joynt, and Mark Rzchowski. The staff at the Wisconsin Synchrotron Radiation Center, especially Dan Wallace, were helpful. Financial support was provided by Ecole Polytechnique Federale Lausanne, Fonds National Suisse de la Recherche Scientifique, and the Wisconsin Alumni Research Foundation.

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